

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-176605

(43)Date of publication of application : 09.07.1996

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(51)Int.Cl. B22F 1/02  
B22F 1/00

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(21)Application number : 06-337078 (71)Applicant : SUMITOMO METAL MINING CO LTD

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## (54) PRODUCTION OF PALLADIUM COATED SILVER POWDER

### (57)Abstract:

PURPOSE: To provide a method for producing palladium coated silver powder, by which particle diameter can be arbitrarily controlled while keeping sharp particle size distribution.

CONSTITUTION: A mixture of L-ascorbic acid with a hydrazine compd. is added as a reducing agent to an aq. soln. of silver-ammine chloride having  $\geq 10\text{g/l}$  concn. of ammonium chloride, silver particles are formed at 30-70°C and the objective palladium coated silver powder is obtd. by coating the silver particles with palladium. The particle size distribution can be controlled to the range of  $0.3\text{-}1.0\mu\text{m}$ .

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### LEGAL STATUS

[Date of request for examination] 14.05.2001

[Date of sending the examiner's decision of rejection] 20.01.2004

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's  
decision of rejection]

[Date of requesting appeal against examiner's  
decision of rejection]

[Date of extinction of right]

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Industrial Application] This invention relates to palladium covering silver dust suitable as a constituent for conductive film formation for forming the electrode of a stacked type ceramic condenser, the circuit of a laminating ceramic substrate, etc., and its manufacture approach.

**[0002]**

[Description of the Prior Art] The green sheet for stacked type ceramic condensers uses dielectrics, such as barium titanate, as a principal component, and the green sheet for laminating ceramic substrates uses an alumina, glass, etc. as a principal component. These principal components are mixed with a binder and a solvent, in order to form a required electrode and a circuit on the green sheet which formed this mixture by the doctor blade method, the roll coater method, etc., the constituent for conductive film formation is applied, and a stacked type ceramic condenser and a laminating ceramic substrate are manufactured by accumulating these [ two or more layers ] and calcinating at 900-1400 degrees C. It depends for this burning temperature on the degree of sintering of a principal component, and a required burning temperature is decided by the principal component.

[0003] This electrode and the constituent for conductive film formation used for a circuit are fused with that burning temperature, does not evaporate, but, moreover, must be able to be burned to the ceramic green sheet concerned. The various silver-palladium alloys with which palladium content differs as an electrical conducting material of such a constituent for conductive film formation corresponding to palladium or burning temperature are used. It enables it to sinter a principal component at low temperature more in the above laminating ceramic products in recent years, and corresponding to it, the electrical conducting material of the constituent for conductive film formation also enables it to use a cheaper silver-palladium alloy with low palladium content, and low-pricing of the laminating ceramic product by cost saving of these both is attained.

[0004] By the way, when manufacturing a silver-palladium alloy and the temperature up of the mixture of the end of silver dust (melting point of 960.5 degrees C) and palladium powder (melting point of 1552 degrees C) is carried out to burning temperature, there is a problem of fusing before silver dust alloys with palladium, forming a minute ball or evaporating. For this reason, the coprecipitation powder of silver-palladium is used for the above-mentioned conductive ingredient. Silver-palladium coprecipitation powder mixes sodium carbonate etc. with the solution mixed with the silver nitrate by the ratio of a request of a palladium nitrate, settles the carbonate of silver and palladium, makes reducing agents, such as formalin, a formic acid, and a hydrazine, act on this, is obtained, and is accepted to be an alloy powder once from the X diffraction Fig. However, if an electrode, a circuit, etc. are formed with the constituent for conductive film formation using this coprecipitation powder, in spite of carrying out specified quantity content of the palladium, the phenomenon which silver is fusing locally is accepted. For this reason, when this coprecipitation powder was used, silver-palladium coprecipitation powder with more how many minute palladium than the predetermined palladium content equivalent to burning temperature had to be used.

[0005] In order to solve such a trouble, this invention persons proposed the manufacture approach of the powder which covered the silver granule child with palladium (JP,1-198403,A). According to this, a silver granule child's front face whose mean particle diameter particle shape is 0.1-2 micrometers in a globular form mostly is covered with palladium, and melting of the silver in the middle of a temperature up and evaporation can be effectively prevented on the occasion of production of said silver-palladium alloy for electrical conducting materials. In addition, such a silver granule child is obtained from chloro diamine silver, a silver nitrate, and silver carbonate by reduction by the thiourea dioxide, the sodium borohydride, formalin, a hydrazine, etc.

[0006] Thus, stability of the presentation of a silver-palladium alloy has desired to control the particle size of palladium covering silver dust. Although the powder which has sharp particle size distribution with a detailed particle size of 0.3 micrometers or less is easily obtained by the approach of said open official report, it is a big size range beyond it, and it is difficult to control particle size to arbitration, with sharp particle size distribution maintained. This is because the particle size of the silver granule child who becomes the heart of palladium covering silver dust is mostly decided by the class of reducing agent. For example, although silver dust with a comparatively big particle size can be obtained if a reducing agent with comparatively weak reducing power like formalin is used, it will be difficult for arbitration to control particle size, and the variation in particle size will become large. If palladium is covered to such silver dust, only palladium covering silver dust with the large variation in particle size will be obtained.

[0007]

[Problem(s) to be Solved by the Invention] The purpose of this invention is made in order to solve the above-mentioned trouble, and it provides arbitration with the manufacture approach of the palladium covering silver dust which can control particle size in 0.3-1.0 micrometers, with sharp particle size distribution maintained. Furthermore, the approach of manufacturing the silver granule child for manufacturing such palladium covering silver dust is offered.

[0008]

[Means for Solving the Problem] In order to solve the above-mentioned trouble, it faces adding a reducing agent to a chlorination ammine silver water solution, and forming a silver granule child, and the magnitude of the silver granule child who becomes the heart by the following approach, and the variation of particle size are controlled by this invention. That is, reduction of chlorination ammine silver is performed using the mixture of L-ascorbic acid and a hydrazine compound, and reduced temperature is made into 30-70 degrees C. Furthermore, it is desirable to make ammonium-chloride concentration in a chlorination ammine silver solution into 10 or more g/l. Thus, palladium is covered to the formed silver granule child, and palladium covering silver dust is obtained.

[0009]

[Function] In this invention, a hydrazine compound and the mixed solution of L-ascorbic acid are used as a reducing agent. As a hydrazine compound, although the mixture of a kind or some kinds can be used among hydrazine hydrate, anhydrous hydrazine, hydrazine sulfate, and hydrazine hydrochloride, the ease of a price and handling to hydrazine hydrate is desirable.

[0010] On the occasion of reduction of silver, the particle size of the silver granule child who becomes the heart of palladium covering silver dust is controlled by this invention by changing the mixing ratio of a hydrazine compound and L-ascorbic acid. As a device in which a silver particle size changes, it thinks as follows by changing the mixing ratio of two kinds of said reducing agents. Reduction of the silver by the hydrazine compound progresses promptly far rather than the case where it is based on L-ascorbic acid. Therefore, in early stages of a reaction, after karyogenesis happens by reduction of the silver by the hydrazine compound and a hydrazine compound is consumed, reduction of the residual silver by L-ascorbic acid advances, and it is guessed that nuclear growth and grain growth take place. If there are few rates of a hydrazine compound, a silver granule child's particle size becomes large with growth of a small number of nuclei, and when there are many rates of a hydrazine compound conversely, and many silver nuclei become, what has a detailed silver granule child will be obtained. Therefore, the particle size of the silver granule child who becomes the heart of palladium covering

silver dust, so that there are few amounts of the hydrazine compound to the silver reaction equivalent becomes large, and a silver granule child's particle size becomes small, so that there are many amounts of a hydrazine compound.

[0011] In addition, although the amount of a hydrazine compound cannot be overemphasized, about the amount of L-ascorbic acid, the amount of it having to be below silver reduction equivalence in which non-returned silver does not remain in a silver reduction process is enough as it. Moreover, the temperature of the reaction mixture in the case of a silver reduction reaction has the desirable range of 30 degrees C - 70 degrees C. When temperature is lower than 30 degrees C and the silver concentration of a chlorination ammine silver solution is high, a silver chloride etc. will re-\*\*\*\*. If the silver chloride which re-\*\*\*\*(ed) is returned, the silver granule child who a configuration and magnitude wrote and became Lycium chinense will be generated and intermingled. Although such a situation is avoidable by lowering silver concentration, productivity worsens and it has a problem economically. Moreover, in a hot case, in order that the vaporization of ammonia may increase from a chlorination ammine silver solution, a silver ammine complex may decompose and a silver chloride etc. may \*\*\*\*, it is not more desirable than 70 degrees C.

[0012] Moreover, the reason for making an ammonium chloride live together in silver reduction reaction time in this invention is because it becomes possible for there to be effectiveness which lengthens time amount, i.e., an induction period, until a reducing agent is added to a silver solution and silver \*\*\*\*, and to press down the variation in particle size low by this. Thus, if an induction period can be lengthened, it can control that a reduction reaction begins in the condition with the uneven mixed state of a chlorination ammine silver water solution and a reducing agent, and, thereby, variation in a silver granule child's particle size can be lessened. The concentration of an ammonium chloride has desirable 10 g/l - 50 g/l. If fewer than 10 g/l, the induction period extension effectiveness is not enough, and in order that a silver granule child may \*\*\*\* in the condition with the uneven mixed state of reaction mixture, only a particle uneven as a result is obtained. In 50 or more g/l, since there is no difference in the description of the particle obtained even if it increases more than it, it is uneconomical. As it is the above, the palladium covering silver dust of the particle size of arbitration is got by covering the palladium of the amount of arbitration by the silver granule child who controlled particle size. Although especially the covering approach of palladium is not limited, after adding a hydrazine compound to a silver granule child's suspension, for example like JP,1-198403,A, approaches, such as holding at 60 degrees C and adding promptly palladium salting in liquid, such as a tetra-ammine palladium solution, are suitable.

[0013]

[Example] An example is indicated below.

(Example 1) The silver content dissolved the silver chloride (product made from Yokozawa Chemistry Metallurgy) equivalent to 18g in 220ml 25% aqueous ammonia (product made from Wako Pure Chem Industry). 4.6g (product made from Wako Pure Chem Industry) of ammonium chlorides was added to this, and solution temperature was held at 40 degrees C. This solution was used as A liquid. On the other hand, 11.3g (product made from Wako Pure Chem Industry) of L-ascorbic acid and 10.5g (the product made from Wako Pure Chem Industry, 2(NH<sub>2</sub>)H<sub>2</sub>O 98%) of hydrazine hydrate were dissolved in 50ml pure water, and solution temperature was held at 40 degrees C. This was made into B liquid.

Subsequently, the silver granule child who uses a metering pump for this, adds, covering B liquid for 5 minutes, and becomes the heart was obtained, stirring A liquid.

[0014] Thus, to the suspension of the obtained silver, again, after adding 30g of hydrazine hydrate, the tetra-ammine JIKURO palladium (Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>) solution with which palladium corresponds [ 1. ] in 50g /was added in 840ml and an instant, and palladium covering silver dust was obtained. In this way, after filtering and dissociating and drying, when it observed after washing the obtained palladium covering silver dust using the scanning electron microscope, the coefficient of variation (standard deviation) of particle size was 0.22 in the mean particle diameter of 0.4 micrometers.

[0015] (Example 2) Palladium covering silver dust was obtained like the example 1 except having changed into 0.02g the amount of the hydrazine hydrate used at the time of reduction of silver. The

mean particle diameter of the silver dust concerned was 0.7 micrometers, and coefficient of variation was 0.28.

(Example 3) Palladium covering silver dust was obtained like the example 1 except having changed into 0.2g the amount of the hydrazine hydrate used at the time of reduction of silver. The mean particle diameter of the silver dust concerned was 0.5 micrometers, and coefficient of variation was 0.24.

(Example 4) Palladium covering silver dust was obtained like the example 1 except having made the ammonium chloride the silver solution in 65g/l. The mean particle diameter of the silver dust concerned was 0.4 micrometers, and coefficient of variation was 0.25.

[0016] (Example 5) Palladium covering silver dust was obtained like the example 1 except having made the silver reduction reaction into 32 degrees C. The mean particle diameter of the silver dust concerned was 0.4 micrometers, and coefficient of variation was 0.26.

(Example 6) Palladium covering silver dust was obtained like the example 1 except having made the silver reduction reaction into 65 degrees C. The mean particle diameter of the silver dust concerned was 0.4 micrometers, and coefficient of variation was 0.27.

(Example 7) Palladium covering silver dust was obtained like the example 1 except having not added an ammonium chloride in a silver solution. Although the mean particle diameter of the silver dust concerned was 0.4 micrometers, coefficient of variation was as large as 0.52.

(Example 8) Palladium covering silver dust was obtained like the example 1 except having made ammonium-chloride concentration the silver solution in 9.5g/l. Although the mean particle diameter of the silver dust concerned was 0.4 micrometers, coefficient of variation was a little as large as 0.38.

[0017] (Example 1 of a comparison) Palladium covering silver dust was obtained like the example 1 except having made only into L-ascorbic acid the reducing agent used at the time of reduction of silver. The mean particle diameter of the silver dust concerned became large with 1.3 micrometers, and coefficient of variation was 0.35.

(Example 2 of a comparison) Palladium covering silver dust was obtained like the example 1 except having made only into hydrazine hydrate the reducing agent used at the time of reduction of silver. The mean particle diameter of the silver dust concerned was as small as 0.25 micrometers, and coefficient of variation was 0.27.

(Example 3 of a comparison) Although it was made to be the same as that of an example 1 except having carried out the silver reduction reaction at 25 degrees C, floc generated and desired palladium covering silver dust was not made.

(Example 4 of a comparison) Although it was made to be the same as that of an example 1 except having carried out the silver reduction reaction at 74 degrees C, floc generated and desired palladium covering silver dust was not made.

[0018] The above result was summarized in Table 1. In addition, in Table 1, the hydrazine equivalent says the hydrazine equivalent to Ag reduction.

[0019]

[Table 1]

The amount of Ag The amount of Pd \*\*\*\* ASUKORUBI Hydrazine NH<sub>4</sub>Cl Hydrazine N acid Equivalent (g) (g) (g) (%) (g/l)

Example 1 18 42 10.5 11.3 500 20 examples 2 18 42 0.02 11.3 1 20 examples 3 18 42 0.02 11.3 10 20 examples 4 18 42 10.5 11.3 500 65 examples 5 18 42 10.5 11.3 500 20 examples 6 18 42 10.5 11.3 500 20 examples 7 18 42 10.5 11.3 500 Zero example 8 18 42 10.5 11.3 500 Example 1 of 9.5 comparisons 18 42 0 11.3 0 Example 2 of 20 comparisons 18 42 10.5 0 500 Example 3 of 20 comparisons 18 42 10.5 11.3 500 Example 4 of 20 comparisons 18 42 10.5 11.3 500 Reduced temperature Particle size

Particle size Coefficient of variation Note (degree C) (micrometer)

Example 1 40 0.4 0.22 examples 2 40 0.7 0.28 examples 3 40 0.5 0.24 examples 4 40 0.4 0.25 examples 5 32 0.4 0.26 examples 6 65 0.4 0.27 examples 7 40 0.4 0.52 examples 8 40 0.4 Example 1 of 0.38 comparisons 40 1.3 Example 2 of 0.35 comparisons 40 0.25 Example 3 of 0.27 comparisons 25 --- --- Example 4 of a floc generation comparison 74 --- --- Floc generation [0020] In addition, in Table 1, the hydrazine equivalent says the hydrazine equivalent to Ag reduction.

[0021]

[Effect of the Invention] Since the approach by this invention is constituted as mentioned above, palladium covering silver dust can be obtained easily, controlling particle size within the limits of 0.3-1 micrometer.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] The manufacture approach of the palladium covering silver dust characterized by returning chlorination ammine silver at the temperature of 30-70 degrees C with the mixture of L-ascorbic acid and a hydrazine compound in the approach of covering palladium to this silver granule child, and obtaining palladium covering silver dust after adding a reducing agent to a chlorination ammine silver water solution and forming a silver granule child.

[Claim 2] The manufacture approach of the palladium covering silver dust characterized by the ammonium-chloride concentration in a chlorination ammine silver water solution being 10g/l. or more in the approach of covering palladium to this silver granule child, and obtaining palladium covering silver dust after adding a reducing agent to a chlorination ammine silver water solution and forming a silver granule child.

[Claim 3] The process of the silver granule child who controls a silver granule child's particle size by adding the mixture of L-ascorbic acid and a hydrazine compound to a chlorination ammine silver water solution, facing returning chlorination ammine silver and generating a silver granule child, and adjusting the mixing ratio of L-ascorbic acid and a hydrazine compound.

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